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use in the silver cell

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The Silver Oxides
Preparation, Analysis, and Use in the Silver Cell

BY

WILLIAM PARKS SHUMAN, JR.

THE SILVER OXIDES
PREPARATION, ANALYSIS, AND USE IN THE SILVER CELL

by
William Parks Shuman, Jr.

A THESIS
Presented to the Graduate Faculty
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1954

Thesis

S492

This thesis is accepted and approved in partial
fulfillment of the requirements for the degree of Master
of Science.

(Date)

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INTRODUCTION

The use of the silver oxide-zinc secondary battery by the U. S. Navy's Bureau of Ordnance stimulated the author's interest in this electrochemical couple. Andre's pioneer work in this field (1,2) had been supplemented by the work of Kinoshita using a silver oxide-iron couple (34,35,36), by the work of Denison using a silver oxide-zinc secondary battery (15), and by the work of White et al using a silver oxide-zinc primary battery (72).

Further study of the silver oxides was dictated by the large amount of conjecture in the literature concerning the chemical and electrochemical behavior of silver oxides. Most of this conjecture revolves around the very existence of some of the reported silver oxides and around the possible molecular formulas for them. A survey of the literature revealed the following possible oxides of silver:

1. AgO (Ref. 6,11,13,14,18,23,30,40,49).
2. Ag_2O_2 (12,18,21,25,26,27,30,37,62).
3. Ag_2O_3 (4,9,12,14,40).
4. $\text{Ag}(\text{AgO}_2)_2$ (43,70).
5. Ag_4O_3 (59,60).
6. Ag_4O (17,19,20).
7. $\text{Ag}_2\text{O}_2 \cdot \text{Ag}_2\text{O}_3$ (44).

This extensive list indicated the amount of previous study that had been made of the silver oxides exclusive of the well-known oxide, Ag_2O . Little of this previous study

removed the anomalies mentioned above. These conjectures could be removed only by a systematic study of the oxides.

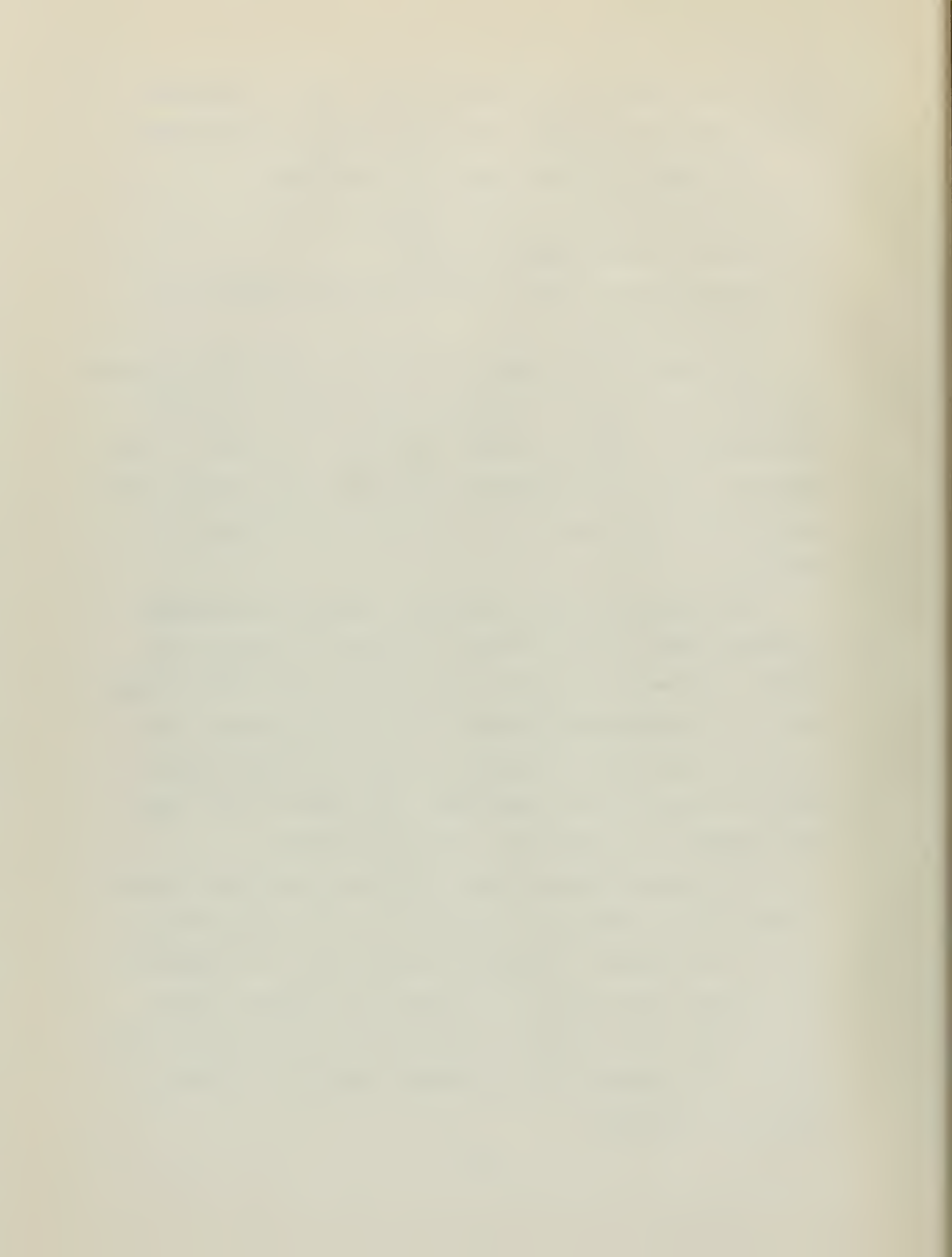
The purpose of this study was three-fold:

1. Preparation of the various oxides.
2. Analysis of the prepared oxides.
3. Electrochemical action of these analyzed oxides in a silver-zinc cell.

The study of the preparation of the oxides was expected to disclose the method or methods that would be the most satisfactory in terms of yield and purity of product. This study was therefore indirectly directed toward revealing the process that might have the most value for quantity production.

The analysis of the compounds prepared was expected to remove some of the previous conjecture concerning the oxides. By determining with some accuracy the silver-oxygen ratio, the exact nature of the oxide was determined. In order to obtain this information, a new "modified Dunas" method of analysis was developed. This part of the study also provided an evaluation of this new method.

The electrochemical study revolved around the reaction of the silver oxides in an electrolytic cell using various rates of discharge. The analysis would make it possible to characterize the reaction as typical of a certain oxide. In addition, the electrochemical characteristic was expected to give some measure of the previous analysis in terms of percentage capacity.



Part I
Preparation of the Oxides

INTRODUCTION

Table I summarizes the many chemical and electrochemical methods for the preparation of silver oxides. An examination of this Table reveals that usually the chemical methods consist of the precipitation of the oxide from a solution of a silver salt by the action of some oxidizing reagent. The electrochemical methods usually consist of the electrolytic oxidation of silver or a silver salt in alkaline solution. In view of the large number of suggested methods of preparation, the decision was made to impose certain limitations on those methods to be studied.

The first and most important limitation was the decision to prepare only those oxides that were true compounds; thus, mixtures or products of incomplete reduction or oxidation were eliminated. This restriction eliminated the study of Ag_2O_3 , Ag_4O_3 , $\text{Ag}(\text{AgO}_2)_2$, $\text{Ag}_2\text{O}_2 \cdot \text{Ag}_2\text{O}_3$ and Ag_4O . The first of these compounds would have a high degree of instability due to the high ionization potential of silver to the plus 3 state, 35.9 electron volts as compared to 21.4 electron volts for the second ionization potential, and 7.574 electron volts for the first ionization potential. The instability of Ag_2O_3 had been confirmed by Jirsa (25) who reported the catalytic decomposition of this oxide by the lower oxides. Dunoyer (17) had proven that Ag_4O was an intermediate in the reduction of Ag_2O . The structure of the three remaining



oxides not studied indicated that they were mixtures, and there was considerable controversy in the literature about their very existence. It was believed, by the author, that these three remaining oxides were essentially mixtures of silver, Ag_2O , and AgO .

The second limitation on the methods of preparation was the decision to use only chemical methods of preparation. The conditions for chemical preparation were often less stringent and the obtained yield indicated the minimum to be expected. Under electrochemical conditions, which were generally more oxidizing, the expected yield would be greater although energy requirements might exceed those of chemical conditions. The possibilities of quantity production would be more clearly revealed by the use of chemical methods.

The third and final limitation was the decision to use those methods that indicated a high yield and a high degree of purity of product. Some of the methods involve silver salts that were less soluble than the silver oxides; hence, these methods would have a poor yield. A high degree of purity could only be obtained by using those reagents that would produce products readily removed upon completion of the reaction.

Table I. Methods of Preparation for the Silver Oxides from the Literature

Oxide	Chemical Methods	Electrochemical Methods
Ag ₂ O	1) AgNO ₃ and NaOH (41,50,55,56,58)	1) Electrolysis of silver arsenate (63)
	2) AgNO ₃ and Ba(OH) ₂ (8,32,50,56,68)	2) Arcing of silver electrodes in water (48)
	3) AgCl and NaOH (56)	3) Cathodic oxidation of silver by silent discharge (22)
	4) Ag ₂ CO ₃ and NaOH (56)	4) Electrolytic oxidation of silver film in NaOH (71)
	5) Oxidation of Ag with O ₃ (31)	5) Electrolysis of NaNO ₃ with silver electrodes (47)
AgO	1) AgNO ₃ , NaOH, and K ₂ S ₂ O ₈ (3,11,30)	1) Anodic oxidation of AgNO ₃ (6,23,49)
	2) AgNO ₃ , NaOH, and K ₂ S ₂ O ₈ (6)	2) Electrolysis of AgNO ₃ and HNO ₃ (52,53)
	3) Ag ₂ O and CO (66)	
	4) Ag ₂ O and formic acid (66)	
	5) AgF and KOH (18)	
	6) Oxidation of silver in acid medium (14)	
	7) Oxidation of silver with PbO ₂ , O ₃ , or Ce ⁺⁴ (31,43,54)	



Table I. (Cont'd.)

Oxide	Chemical Methods	Electrochemical Methods
Ag_2O_2	1) AgNO_3 and $\text{K}_2\text{S}_2\text{O}_8$ (12) 2) AgNO_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (29,30,33) 3) AgNO_3 and H_2O_2 (45) 4) Energetic oxidation of silver and silver salts (25,31) 5) AgNO_3 and F_2 (18,21)	1) Anodic oxidation of silver in alkali (24,25,31,40)
Ag_2O_3	1) Oxidation of silver in acid (14) 2) Reaction of AgO and HNO_3 (4) 3) AgNO_3 and $\text{K}_2\text{S}_2\text{O}_8$ (aqueous) (12) 4) AgNO_3 and $\text{K}_2\text{S}_2\text{O}_8$ (pyridine) (5,6)	1) Anodic oxidation of soluble silver salts (9,25) 2) Electrolysis of AgNO_3 and Ag_2SO_4 (40)
$\text{Ag}(\text{AgO}_2)_2$		1) Electrolysis of AgNO_3 (7,10)
Ag_4O_3		1) Electrolysis of silver electrode in dilute alkali (59,60)
Ag_4O	1) Reduction of Ag_2O at 50-100° (17,20)	
$\text{Ag}_2\text{O}_2 \cdot \text{Ag}_2\text{O}_3$	1) Ag_2SO_4 and $\text{K}_2\text{S}_2\text{O}_8$ (44)	

EXPERIMENTAL

The three oxides prepared were Ag_2O , AgO , and Ag_2O_2 . Two methods of preparation were attempted for each oxide using procedures suggested from the literature. As a result of preparing the oxides by two entirely different methods, the yields could be compared. A check was made by X-ray diffraction patterns to determine whether the resulting oxides had the same crystallographic structure.

The sensitivity of the oxides to light had been reported (68). The oxides were then prepared in a three neck flask covered with a heating mantle. The purpose of the mantle was to minimize any light sensitivity that the oxides might have had.

Washing by decantation was used throughout to avoid any losses due to the adherence of the fine particles to the filter. Most procedures had recommended the usual filtration method of separation of the oxides.

All precipitates were dried in vacuo in order to lower the drying temperature. The oxides of silver have a rather low decomposition temperature, $350-420^\circ\text{C}$. (21), and a change in crystal structure at 132°C . had also been reported (60). There is a tendency for the oxides to retain some residual moisture (40,56) and this phenomena had been said to be due to a surface film of AgOH (56). Drying under a vacuum aided the removal of water and reduced the possibility of partial decomposition.



The procedures used were as follows:

1. Ag_2O

Procedure A:

85 grams of AgNO_3 in 250 ml. of water were added by drops and with constant stirring to a boiling ($104^\circ\text{C}.$) solution of 22.5 grams of NaOH in 262 ml. of water. Time of addition was 15 minutes and time of reaction, or stirring, was 2 hours. The precipitate was washed thoroughly by decantation and dried in vacuo at $80^\circ\text{C}.$ for 24 hours.

Procedure B:

21.35 grams of AgNO_3 in 250 ml. of water were added by drops and with constant stirring to a solution of 10.71 grams of $\text{Ba}(\text{OH})_2$ in 250 ml. of water at $80^\circ\text{C}.$ Time of addition was 15 minutes and time of reaction, or stirring, was 2 hours. The precipitate was washed by decantation and dried in vacuo at $80^\circ\text{C}.$ for 24 hours.

2. AgO

Procedure A:

72 grams of NaOH and 75 gm. of $\text{K}_2\text{S}_2\text{O}_8$ in 200 ml. of water were added to 125 ml. of water at $85^\circ\text{C}.$ 51 grams of AgNO_3 in 200 ml. of water were added by drops and with constant stirring, maintaining the temperature at $90^\circ\text{C}.$ Time of addition was 15 minutes and time of reaction, or stirring, was 2 hours. The precipitate was washed by decantation and dried in vacuo at $80^\circ\text{C}.$ for 24 hours.



Procedure B:

72 grams of NaOH were added to one liter of water at 85°C. To this solution were added 75 grams of $K_2S_2O_8$ in an aqueous slurry. 51 grams of $AgNO_3$ in a minimum amount of water were added with constant stirring. The temperature was raised to 90°C. and stirring continued for 15 minutes. The precipitate was washed by decantation with slightly alkaline water (NaOH) and dried in vacuo at 75°C. for 24 hours.

3. Ag_2O_2

Procedure A:

30 grams of $AgNO_3$ in 150 ml. of water were added with constant stirring to 50 grams of $K_2S_2O_8$ in 500 ml. of water at room temperature. Stirring was continued for 2 hours and the precipitate was allowed to settle for 2 hours. It was then washed by decantation and dried in vacuo at 80°C. for 24 hours.

Procedure B:

29.5 grams of $(NH_4)_2S_2O_8$ in sufficient water to dissolve were added cautiously by drops and with constant stirring to 42.5 grams of $AgNO_3$ in 382.5 ml. of water at room temperature. Stirring was continued for 2 hours and the precipitate was allowed to settle for 2 hours. It was then washed by decantation and dried in vacuo at 80°C. for 24 hours.



RESULTS OF PREPARATION OF SILVER OXIDES

Table II gives the yields obtained by each method of preparation. An examination of the Table reveals that method A for each oxide had the highest yield. Method A for Ag_2O was the precipitation of the oxide from AgNO_3 solution with NaOH solution. Method A for AgO was the precipitation of the oxide from AgNO_3 solution with NaOH and $\text{K}_2\text{S}_2\text{O}_8$ solution. Method A for Ag_2O_2 was the precipitation of the oxide from AgNO_3 solution with $\text{K}_2\text{S}_2\text{O}_8$ solution. The low yields can be explained by incomplete oxidation of the silver, losses incurred in washing, and by the slight solubility of the oxides.

Table II. Yield Obtained with Each Method of Preparation

Compound	Procedure	Yield
Ag_2O	A	99%
Ag_2O	B	53%
AgO	A	98.5%
AgO	B	82.5%
Ag_2O_2	A	73.5%
Ag_2O_2	B	71%

All of the precipitates were very fine powders varying in color from dark grey to black. The precipitate obtained by the use of Ba(OH)_2 (Procedure B for Ag_2O) was dark brown in color, thus differing from the others and indicating a difference in particle size.



An attempt was made to precipitate the oxide using AgCl (55) which resulted in the formation of a very fine silver powder. This result confirms the statement that precipitation methods from slightly soluble silver salts would be unsatisfactory.



Part II
Analysis of the Silver Oxides

INTRODUCTION

The anomalous behavior of the silver oxides has been largely due to the many literature references. Often the statement can be found that "this oxide was probably ...", or "this oxide exhibited the behavior of . . .". The evidence supporting such statements were obtained by qualitative or pseudo-analytical means.

Qualitative tests for the higher oxides have been mentioned in the literature by Salkowski (62) and by Jirsa and Jelinek (31). The method described by Salkowski consisted of the deposition of a fine mirror as a result of boiling the oxide with an excess aqueous solution of an amino fatty acid and the formation of a deep brown solution when the oxide is covered with HNO_3 , the solution becoming colorless upon heating. The qualitative test of Jirsa and Jelinek was the evolution of O_2 by treatment with pure water and the liberation of I_2 from a KI solution by the oxide.

Quantitative tests have been reported by Malaguti (44), who determined the silver-oxygen ratio by treatment of the oxide with FeSO_4 or $\text{H}_2\text{C}_2\text{O}_4$ in H_2SO_4 solution. The results of that method were reported as comparable to those obtained by Malaguti and Barbieri (6) in which the excess H_2O_2 , after addition to the oxide, was determined by titration with KMnO_4 , and the silver was determined by KSCN titration. A quantitative test is described by Jirsa (26) who determined the



amount of oxygen by measurement of the nitrogen given off after decomposition of the oxide with hydrazine hydrate. He further determined the silver content by ignition and weighing.

All of the above analytical methods involved the reaction of the oxide with some other reagent with all the inherent errors. A method was sought which would be free of these errors and which would not depend on any chemical action between the oxides and another reagent. The result was obtained by the use of a "modified Dumas procedure" with confirmation of similar crystallographic structure by the use of X-ray diffraction patterns.

Although a number of studies of the X-ray diffraction patterns of the common oxide Ag_2O have been made by Tiapkina and Dankov (67), Niggli (51), Davey (10) and Wyckoff (73) with subsequent cataloguing of its diffraction pattern, little work has been done on the higher oxides. Braekken (9) states that the exact structure of Ag_2O_3 cannot be determined, again confirming the instability of this oxide. Denison (15) used X-rays to study the plates in a cell during charge and discharge, the cell consisting of silver oxide and zinc plates. No other work has been done on the higher oxides in X-ray studies.

In view of the lack of X-ray studies on other silver oxides besides Ag_2O , a decision was made to use X-ray diffraction patterns as an additional check on the prepared

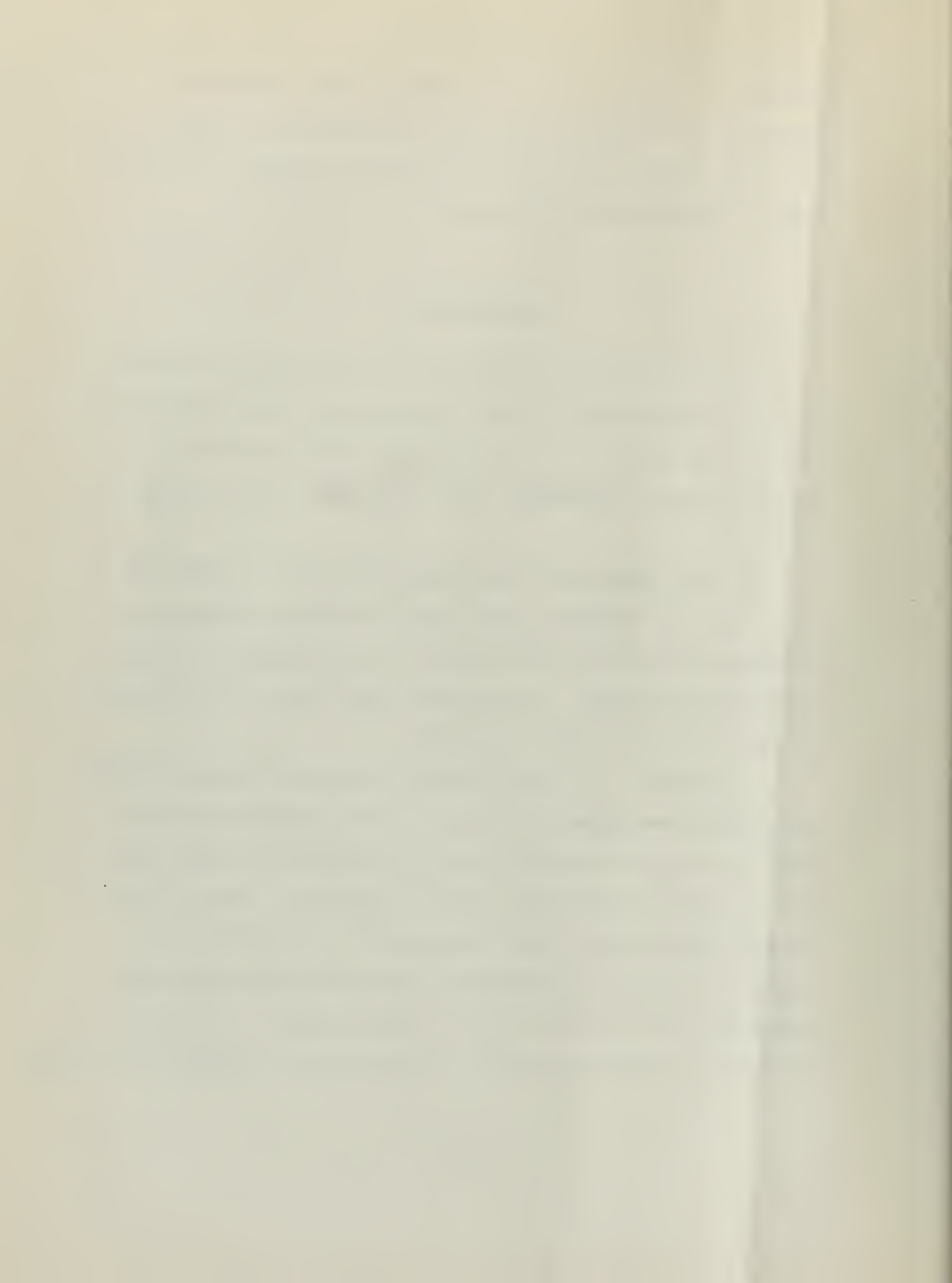
compounds. The use of a sound and accurate analytical technique, coupled with the X-ray diffraction patterns, would do a great deal in removing the previous dilemma of insufficient and inconclusive evidence.

EXPERIMENTAL

The decision to use only physical methods of analysis for the determination of the silver-oxygen ratio led to the use of a new method of analysis which might be called a "modified Dumas procedure". The apparatus used is shown in Fig. 1.

The CO₂ generator was a Dewar flask filled with dry ice. From the generator, CO₂ could be passed through the combustion tube and to the buret, or to the atmosphere by a three-way stopcock. In addition, the supply of CO₂ could be shut off at the first stopcock.

A porcelain boat was heated to constant weight, filled with oxide, reweighed, and placed in the combustion tube. Carbon dioxide was passed through the combustion tube and into the buret filled with 40% KOH solution. When all of the gas entering the buret was adsorbed, indicating the complete removal of atmospheric gases, the CO₂ supply was closed and the combustion tube heated gently. Caution was exercised so that the combustion tube was not heated too rapidly,



as evolution of oxygen and absorbed water could have caused sputtering of the oxide.

When all of the oxygen was driven off, as indicated by the cessation of gas bubbles in the KOH solution, the flame was removed and the CO₂ supply opened to sweep out any remaining oxygen in the combustion tube. Again the complete removal of oxygen was indicated by the complete absorption of the CO₂ by the KOH solution. The KOH solution was then isolated by means of the three-way stopcock. The volume of oxygen was read from the graduated buret after equalizing internal pressure with atmospheric pressure by means of the leveling bulb. The porcelain boat was removed and reweighed, the material remaining in the boat being pure silver.

In using this method of analysis, a minimum of five runs were made on each of the oxides prepared, in addition to runs made on a sample of Ag₂O obtained commercially. The sample size varied from 54 mg. to 195 mg. with the average being about 95 mg. All weighings were to the nearest 0.1 mg. All volumes were read to the nearest 0.01 ml.

The moles of oxygen were obtained by assuming the ideal gas law at the temperature and pressure used. The temperature was obtained from a thermometer that was supported from the buret. The pressure used was that obtained from the existing atmospheric conditions after correction.

X-ray diffraction patterns were taken of all preparations and of the commercial sample, using powder techniques. A General Electric Spectrogoniometer was used for this part of the work and the radiation used was Cu K alpha.

In addition to the patterns taken of the above preparations, patterns were also taken of plates in an electrochemical cell when it was in the charged condition. These latter patterns were taken of the plates themselves which were of a size to fit into the normal powder holder.

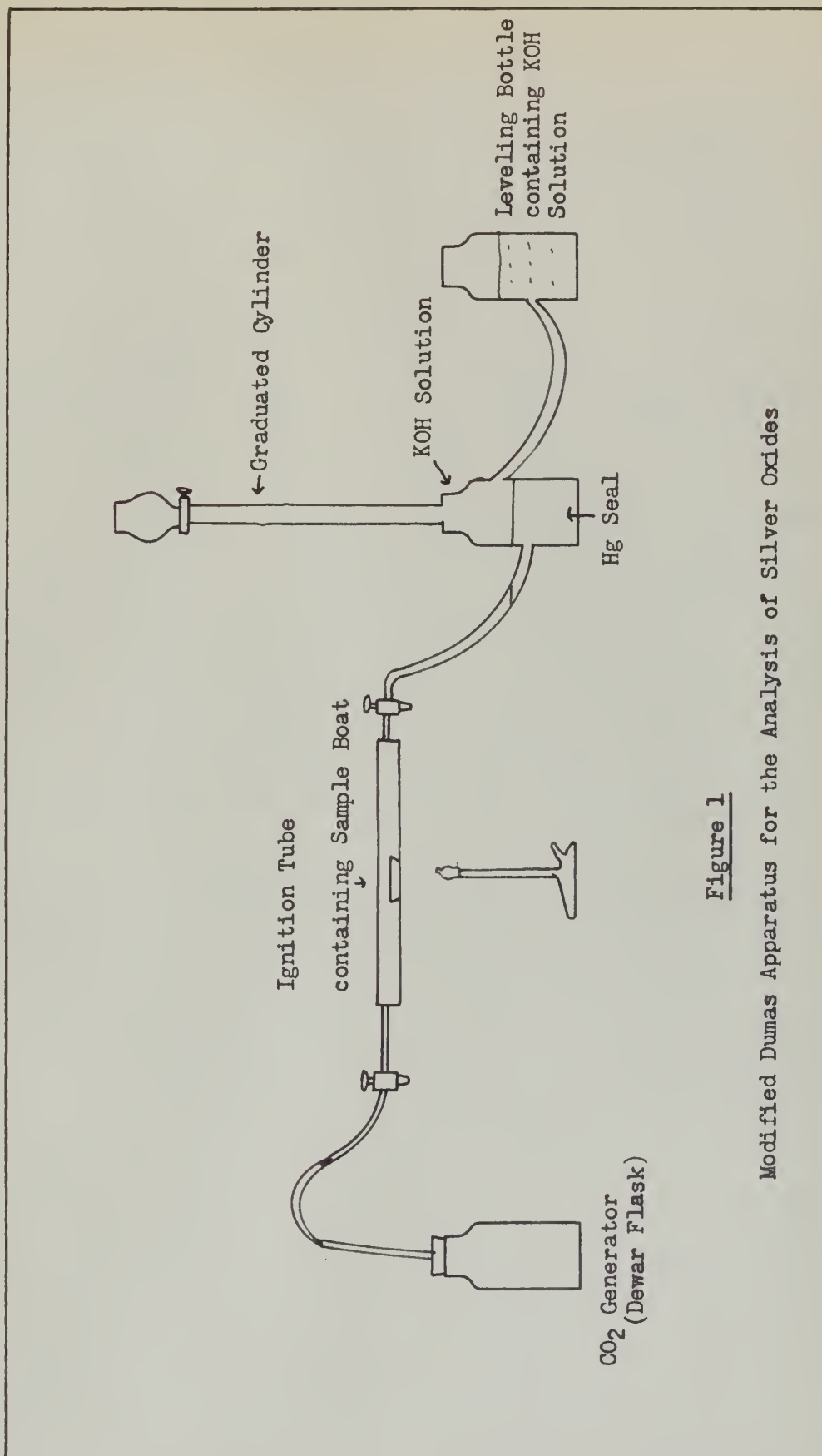


Figure 1

Modified Dumas Apparatus for the Analysis of Silver Oxides

RESULTS OF ANALYSIS OF SILVER OXIDES

The results of the analyses made are summarized in Table III. The results of the X-ray diffraction patterns are reproduced in Figures 2 through 11 (Appendix).

Table III. Results of Analysis of Silver Oxides

Oxide	Method of Prep.	% Ag	Std. Dev.	%O	Std. Dev.	Ag/O Ratio	Std. Dev.
Ag ₂ O	Comm.	91.64	0.10	6.529	0.042	2.082	.013
Ag ₂ O	A	91.23	0.103	6.910	0.104	1.958	.005
Ag ₂ O	B	92.33	0.079	5.391	0.099	2.538	.034
AgO	A	89.66	0.285	9.329	0.218	1.425	.033
AgO	B	88.10	0.178	11.20	0.226	1.167	.009
Ag ₂ O ₂	A	95.76	0.563	0.825	0.017	17.22	.548
Ag ₂ O ₂	B	98.42	0.444	0.666	0.050	21.92	1.813

A detailed examination of Table III reveals a number of interesting facts. The inherent accuracy of this method of analysis was excellent. The standard deviations in general were less than 0.3%. In those cases where larger deviations were found, it was noted that they occur in the silver column and could be a result of sputtering of the oxide while being heated. On the other hand, the standard deviations of the oxygen were spread over a narrower range.

The next item of importance to be learned from Table III was the odd silver-oxygen ratio for all the oxides. None of the ratios obtained approached the stoichiometric

with the exception of the commercial preparation, Ag_2O by method A, and AgO by method B. This anomaly could be explained by the presence of excess silver in the Ag_2O preparations, and by the presence of excess silver and some Ag_2O in the AgO preparations and the Ag_2O_2 preparations.

The presence of excess silver and Ag_2O was confirmed by a detailed comparison of the X-ray patterns for the higher oxides with those patterns for silver and Ag_2O . The diffraction pattern of AgO had a relatively small number of the lines from silver and Ag_2O . On the other hand, the Ag_2O_2 pattern consisted almost entirely of the lines from silver, Ag_2O , and AgO .

From the appearance of the X-ray patterns for Ag_2O_2 , and from the results of the analysis, the important observation was made that Ag_2O_2 was not a true chemical compound but a mixture of the other oxides with metallic silver. An examination of the Ag/O ratio made this readily apparent. This conclusion was further confirmed by the wide variation in the standard deviation of the Ag/O ratio indicating that the oxide was a mixture with the composition varying from sample to sample in the analysis.

Another result of this analysis was the confirmation that method A was the best method of preparing Ag_2O . The value of this method of preparation was indicated by the results of the analysis in terms of purity of product coupled with the findings in Part I that this same method also had the highest yield.

A dilemma was reached in trying to find the best method for preparing AgO. The results of the analysis indicated that method B gave the purer product. The results from Part I, on the contrary, indicate that method A gave the highest yield. Bailar (3), who prepared AgO by method B, obtained a slightly higher yield than the yield obtained by the author, 94% as compared to 82.5%. The conclusion was reached that the use of Bailar's method or method B gave the desired results, a high purity of product and a substantial yield. The slightly lower yield was outweighed when the purity of the product was considered.

Part III
Electrochemical Reactions

INTRODUCTION

As previously noted, some work has been done on the electrochemical reactions of the silver oxides by Andre, Kinoshita, Denison, and White. Other work has been done by Jirsa (28) on the iron-silver couple, Linden (38) on the silver-zinc, Veselovskii (69) on the silver-silver oxide, Martinez (46) on the silver-colloidal silver, Benson and Harrison (7) on the silver-zinc, Makolkin (42) on the hydrogen-silver oxide and Rollet (59) on the mercury-silver oxide couple. A number of patents exist on the zinc-silver oxide couple (2,16) as a source of emf. Other studies have been made on polarization, capacity losses, temperature effects, and kinetics of the silver oxide system by Schmidt and Prening (64), Tanaka (65), Noyes et al (52,53,54), Hickling and Taylor (24), and Lingane and Larson (39).

Much of the above work lacked a systematic method of characterizing the electrochemical characteristics of the individual oxides. It was, as has been previously stated, the overall purpose of this study to remove some of the conjecture concerning the behavior of these oxides. The use of the analyzed oxides in an electrochemical cell at various rates of discharge was designed to give results that could then be attributed to specific preparations.

EXPERIMENTAL

The oxide of each type, Ag_2O , AgO , and Ag_2O_2 , that had the highest degree of purity was used in making a plate for an electrochemical cell. These plates were made by pressing the oxide under 1000 psi. pressure on a silver mesh which had been made damp with KOH solution. A silver wire for the lead had previously been woven through the mesh. The size of the plate was 3.8 x 1.3 cm (1-1/2 x 1/2 in.) after forming.

This pressed plate as one electrode and a zinc plate of the same size as the other electrode were assembled in a cell. The cell was made in two sections to facilitate the removal of the separator which was untreated cellophane. The electrolyte used was a 40% solution of KOH (1.4 specific gravity). The zinc plate was made from sheet zinc, and its thickness was such that the capacity of the cell would not be limited by the amount of zinc.

These assembled cells were then discharged at varying rates of discharge using an Esterline-Angus recorder for continuous recording of the voltage across the cell. The cells using Ag_2O_2 were discharged at only three rates in order to confirm the observations previously made; that is, to show that this oxide was a mixture and not a true chemical compound. In addition, some of the cells were charged until gassing began, and then discharged. This latter procedure

was used in order to make certain that there was a complete conversion in the plate to the oxide normally found in the cell in the charged condition.

X-ray patterns were taken of the plates of the charged cell. This examination was made in order to characterize the oxide normally found in the charged condition.

RESULTS OF ELECTROCHEMICAL ACTION OF SILVER OXIDES

Inasmuch as the active material in the plates varied from discharge to discharge, Table IV shows this variation. In addition, Table IV shows theoretical capacity for each discharge, percent theoretical capacity attained, open circuit voltage, and closed circuit voltage.

Table IV. Values of Discharge Rate, Theoretical Capacity, and Percent Theoretical Capacity Attained for All Discharges

Oxide	Meth. Prep.	Wt. Material	Act. Dischg. Rate amps	Theo. Cap.AH	% Theo. Cap.	O.C.V.	C.C.V.
Ag ₂ O	A	2.920	0.05	0.675	82	1.600	1.52
Ag ₂ O	A	3.348	0.10	0.774	80	1.575	1.475
Ag ₂ O	A	2.633	0.20	0.610	77	1.580	1.45
Ag ₂ O	A	2.629	0.30	0.608	76	1.550	1.38
Ag ₂ O	A	2.457	0.40	0.568	67	1.585	1.35
Ag ₂ O	A	4.370	0.50	1.020	69.3	1.560	1.27
Ag ₂ O	A	3.646	0.80	0.843	51	1.600	1.33
Ag ₂ O	A	2.910	1.00	0.672	14	1.56	1.18
AgO	B	1.507	0.05	0.652	71	1.84	1.55
AgO	B	1.844	0.10	0.798	75	1.70	1.54
AgO	B	1.981	0.20	0.860	78	1.60	1.50
AgO	B	2.025	0.30	0.877	71.5	1.59	1.49
AgO	B	2.395	0.40	1.070	64	1.59	1.48
AgO	B	2.206	0.50	0.955	54	1.61	1.41
AgO	B	2.496	0.80	1.08	19.3	1.77	1.39
AgO	B	2.040	1.00	0.882	59.5	1.62	1.34
Ag ₂ O ₂	A	2.897	0.03	0.670	20.5	1.56	1.40
Ag ₂ O ₂	A	2.452	0.20	0.568	14.0	1.78	1.49
Ag ₂ O ₂	A	1.468	0.10	0.341	58	1.85	1.52

In Table IV all capacities for Ag_2O were based on a Faraday per gram mole basis, and for AgO all capacities were based on two Faradays per gram mole basis. The capacities for Ag_2O_2 could not be estimated on either basis, inasmuch as its exact composition was unknown; however, values were given on the basis of one Faraday per gram mole.

Figures 12-15 (Appendix) show the voltage characteristics of the different oxide plates during discharge. Fig. 16 (Appendix) shows the variation in capacity with load for Ag_2O and AgO .

An examination of the discharge curves for Ag_2O_2 revealed that the capacity of that oxide was quite limited as might have been expected from the analysis. This limited capacity was another confirmation that Ag_2O_2 was not a true compound but was a mixture of silver, Ag_2O , and AgO . The latter must have been present in order for the battery to have such a high open circuit voltage. The theoretical voltage for Ag_2O -Zn is only 1.58 while Ag_2O_2 showed the characteristic of AgO by having an open circuit voltage that approached the theoretical for AgO , 1.88 volts.

An examination of the discharge characteristic of Ag_2O revealed the constant voltage that the cell maintained throughout most of the discharge. The theoretical voltage was 1.58 volts, and all experimental cells were near this value. Those voltages which differed from this value were probably caused by the presence of AgO or metallic silver.

These results confirmed the analysis previously made, in that, the compound as prepared had some impurity of metallic silver.

The most striking voltage characteristic was the difference between that of AgO and the charged cell. Although the open circuit voltage of the chemically prepared AgO approached that of the charged cell, apparently the small amount of impurity present was sufficient to cause this higher voltage to be unstable under load. It was noted, however, that the actual capacities of the chemically prepared oxide were very high in terms of two Faradays per gram mole of oxide.

The high initial voltage of the charged cell was due probably to the complete conversion of the plate to the AgO state. The X-ray patterns taken of the charged plate confirmed this supposition, as there were fewer lines present of silver and Ag₂O than in the chemically prepared compound. The shorter relative length of stability of this higher voltage was probably due to the reduction of AgO by Ag₂O as the latter is formed. The rate controlling factor, kinetically, was apparently the conversion of the higher oxide to the lower oxide. The lower voltage which did occur after the initial high voltage was probably due to the complete conversion of the surface of the plate to Ag₂O. The cell would then exhibit the voltage that was characteristic of Ag₂O.

Part IV
Discussion and Summary

This systematic study of Ag_2O , AgO , and Ag_2O_2 has helped to clarify the behavior of these oxides. Although no work was done on the other oxides reported, Ag_2O_3 , $\text{Ag}(\text{AgO}_2)_2$, Ag_4O_3 , Ag_4O , and $\text{Ag}_2\text{O}_2 \cdot \text{Ag}_2\text{O}_3$, the existence of these as true chemical compounds is unlikely due to the methods of analysis and evaluation previously employed.

The first important finding deduced in this study was that Ag_2O_2 was not a true chemical compound. The analysis of the preparations for this oxide and the accompanying X-ray diffraction patterns confirmed this fact. Further confirmation was obtained by the electrochemical action of this supposed oxide in a cell where it showed the characteristics of AgO , Ag_2O , and Ag . Although only two methods of preparation were used, it is believed that other procedures would lead to the same result; the only variation would be in the relative amounts of Ag , Ag_2O , and AgO in the mixture.

A comparison between the various methods of preparation of the oxides was made. Method A, the precipitation of Ag_2O from AgNO_3 solution by the use of NaOH solution, gave the best results for the preparation of this oxide in terms of yield and degree of purity. In the preparation of AgO , method A, the precipitation of the oxide from AgNO_3 solution by the use of NaOH and $\text{K}_2\text{S}_2\text{O}_8$ solution, differed from method B only in the relative amount of water used. The yield by method B, which was the procedure recommended by Bailar (3), was lower than that reported heretofore. This method, however, had the highest degree of purity and therefore this method appeared best.

It was also found that some of the suggested methods in the literature were not feasible for the preparation of Ag_2O . This finding was due to the attempt to precipitate a more soluble salt from a less soluble salt. The attempt to precipitate Ag_2O from AgCl might have been predicted to be unsuccessful from a more critical examination of the solubility product constant. This predicted result would lead to the likelihood that the preparation from Ag_2CO_3 might also be unsuccessful.

The variation in the silver-oxygen ratio for the oxides prepared is explained in terms of an excess of metallic silver for the Ag_2O compounds and in terms of silver and Ag_2O for the AgO compounds. This explanation was confirmed by the X-ray patterns and by the electrochemical behavior of the oxides in a cell, that is to say, the cells did not reach the capacity that might have been expected if they were true compounds with no impurities. The variation in silver-oxygen ratio from the stoichiometric was only slight for Ag_2O , indicating the greater stability for this oxide under the proper conditions of preparation. The greater variation in the silver-oxygen ratio for AgO indicates the strong oxidizing conditions needed for its preparation and its greater instability. As a result of this observation, it is doubtful that this oxide can be prepared in the pure form by chemical methods unless extreme oxidizing conditions are used. The preparation of this oxide by electrochemical methods seems to be the best way if a product with high purity is desired.

Another important result of this study is the development of a new method of analysis for silver oxides. The "modified Dumas procedure" lends itself to those applications where rapid determinations of the metal-oxygen ratio is needed. It is limited in its applications, however, to those oxides that have a relatively low decomposition temperature. Since the complete reduction temperature of silver oxide was around 400°C. (22), this procedure was admirably suited for the determinations required. The use of X-ray diffraction patterns in this part of the study was merely to ensure that the same compound from each method of preparation was being studied analytically. The inherent lack of errors by the use of this strictly physical method of analysis should lead to its superceding the older physico-chemical methods of analysis with their inherent errors of solubility, side reactions and incomplete reactions.

The electrochemical study, in addition to confirming some of the previous observations, showed that there is a high peak voltage at the start of the discharge when all of the active material in the silver oxide plate is in the form of AgO. Although it might be possible that this high peak voltage may be caused by adsorbed oxygen on the plate, the reproducibility of the voltage in the fully charged state makes this unlikely. This ability to reproduce the peak voltage indicates that the phenomenon is entirely chemical - the conversion of Ag₂O to AgO - and not any

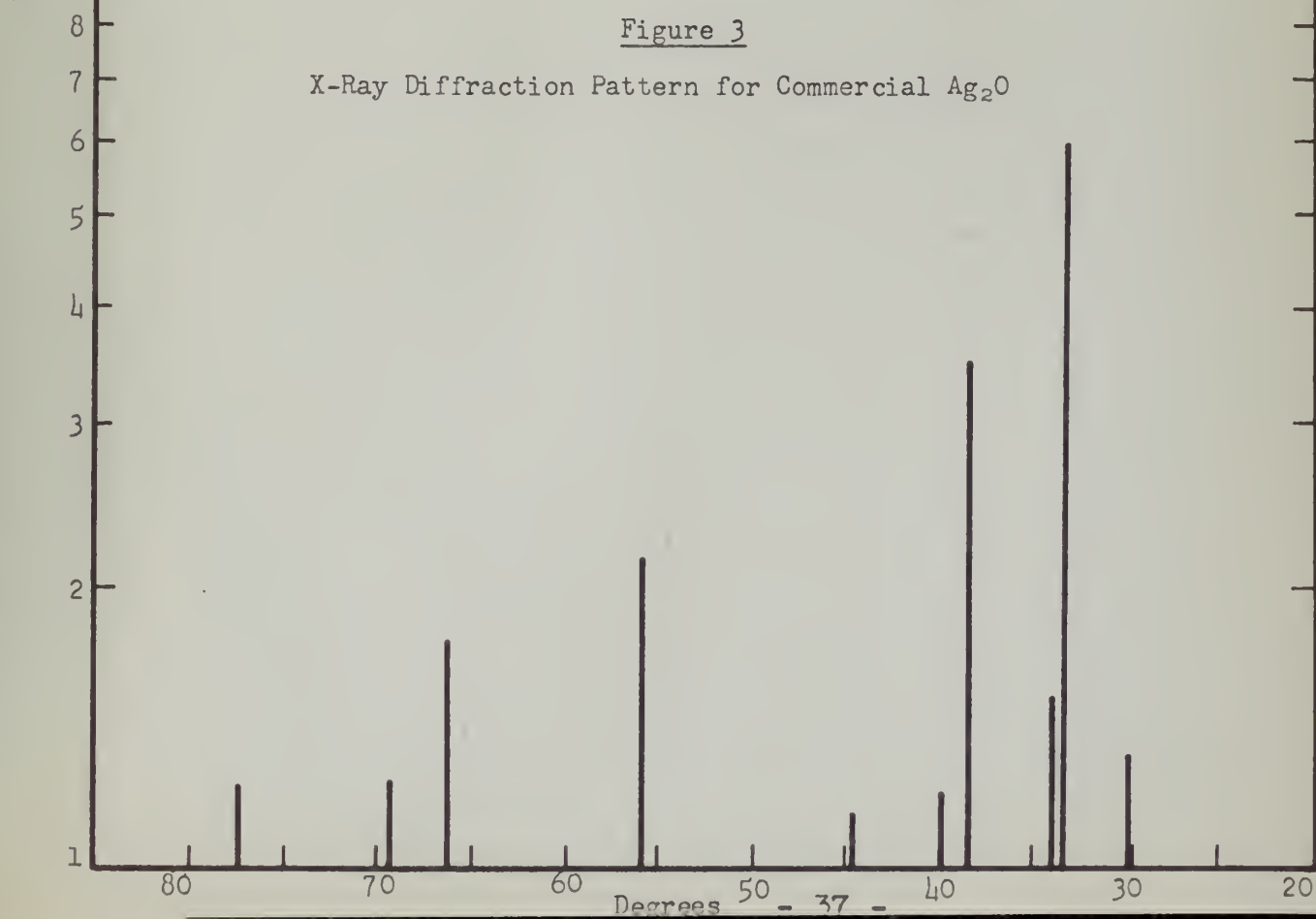
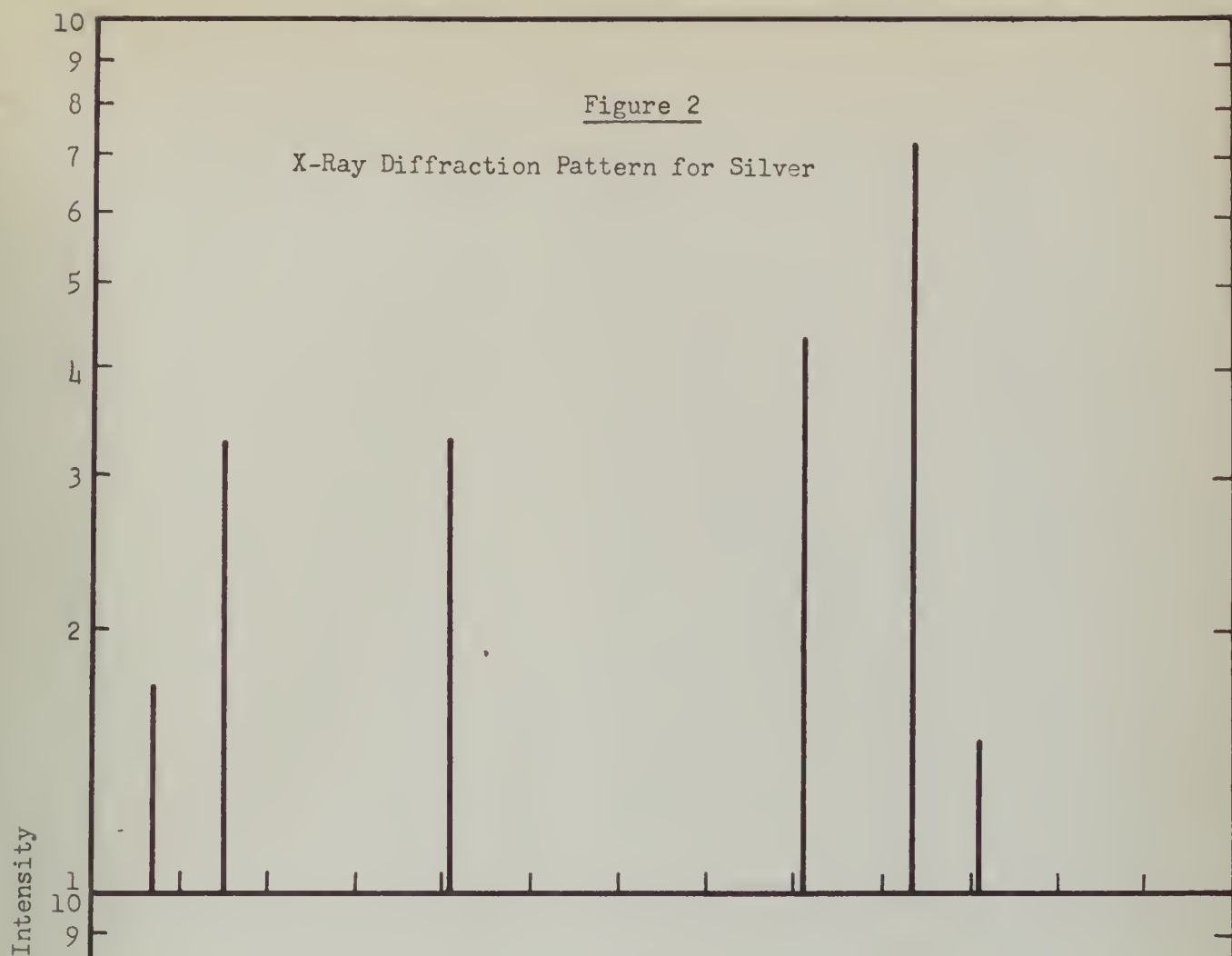
physical phenomenon. X-ray patterns of the charged plates, in which some of the lines of the impurities found in the chemically prepared compound have disappeared, appears to confirm complete oxidation of silver to the plus 2 state. This fact is further confirmed by the fact that the cell delivers almost two Faradays per gram mole of oxide when fully charged. For a physical phenomenon, one Faraday per gram mole would be expected.

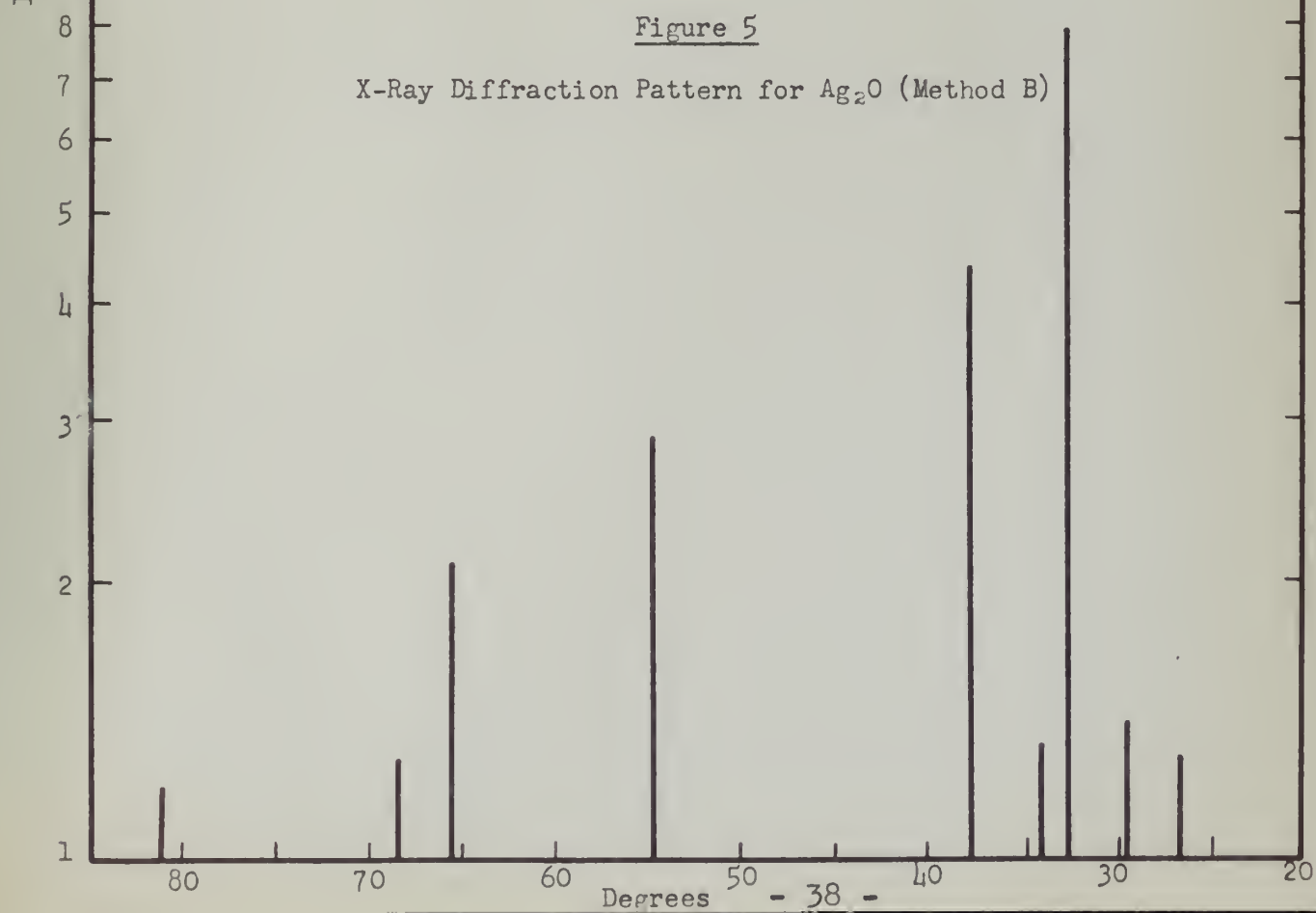
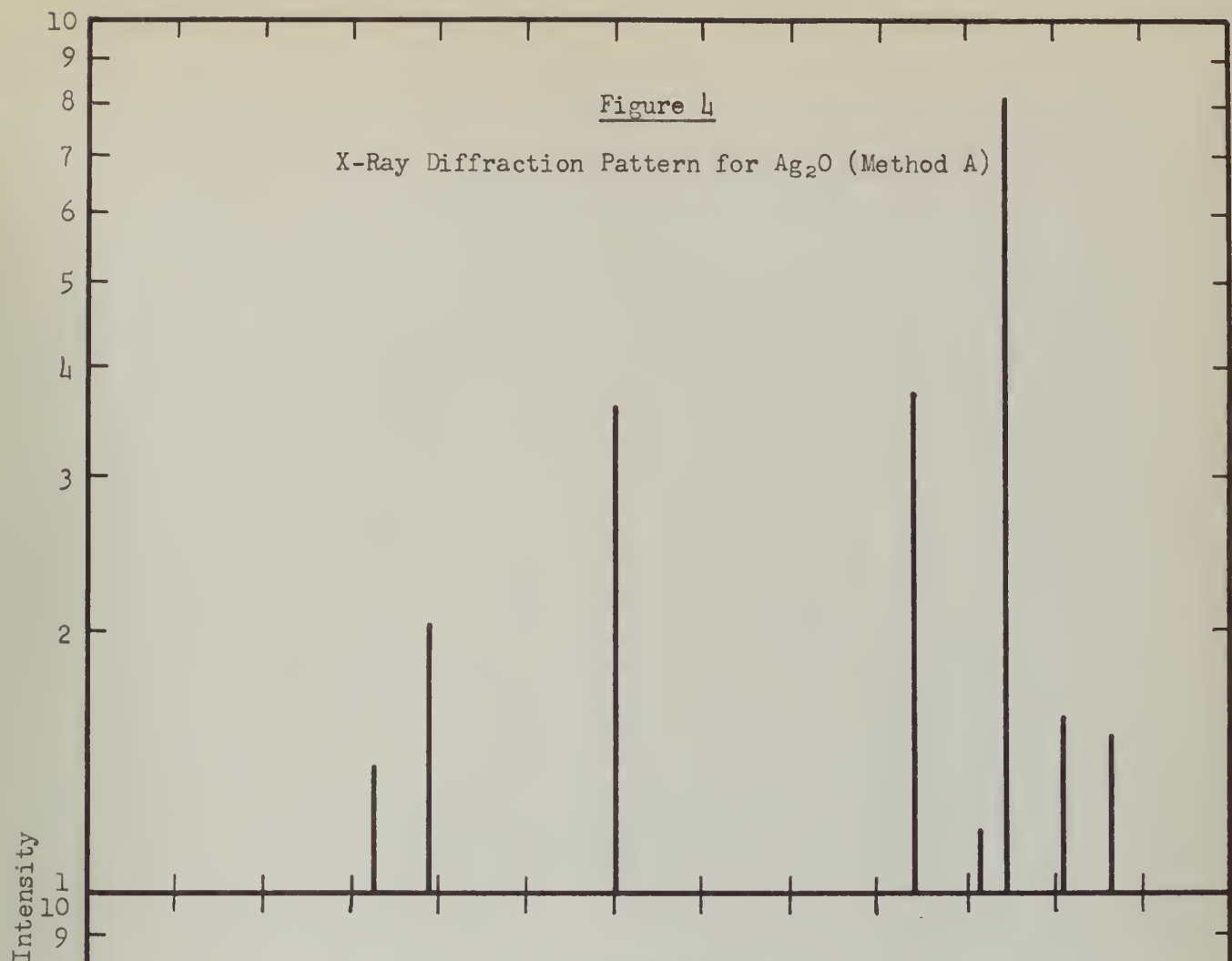
An explanation for the variation in the percent theoretical capacity attained, as shown in Fig. 16, is difficult. The decrease in capacity at higher rates of discharge could be attributed to polarization of the zinc plate, but no attempt was made during discharge to confirm this. The decrease at low rates of discharge for AgO might be explained by the catalytic decomposition of the higher oxide by the Ag₂O present. At low rates of discharge, this phenomenon would have sufficient time to decrease the expected capacity whereas at high rates of discharge this phenomenon would have less time to be felt thus accounting for the increase in percent capacity.

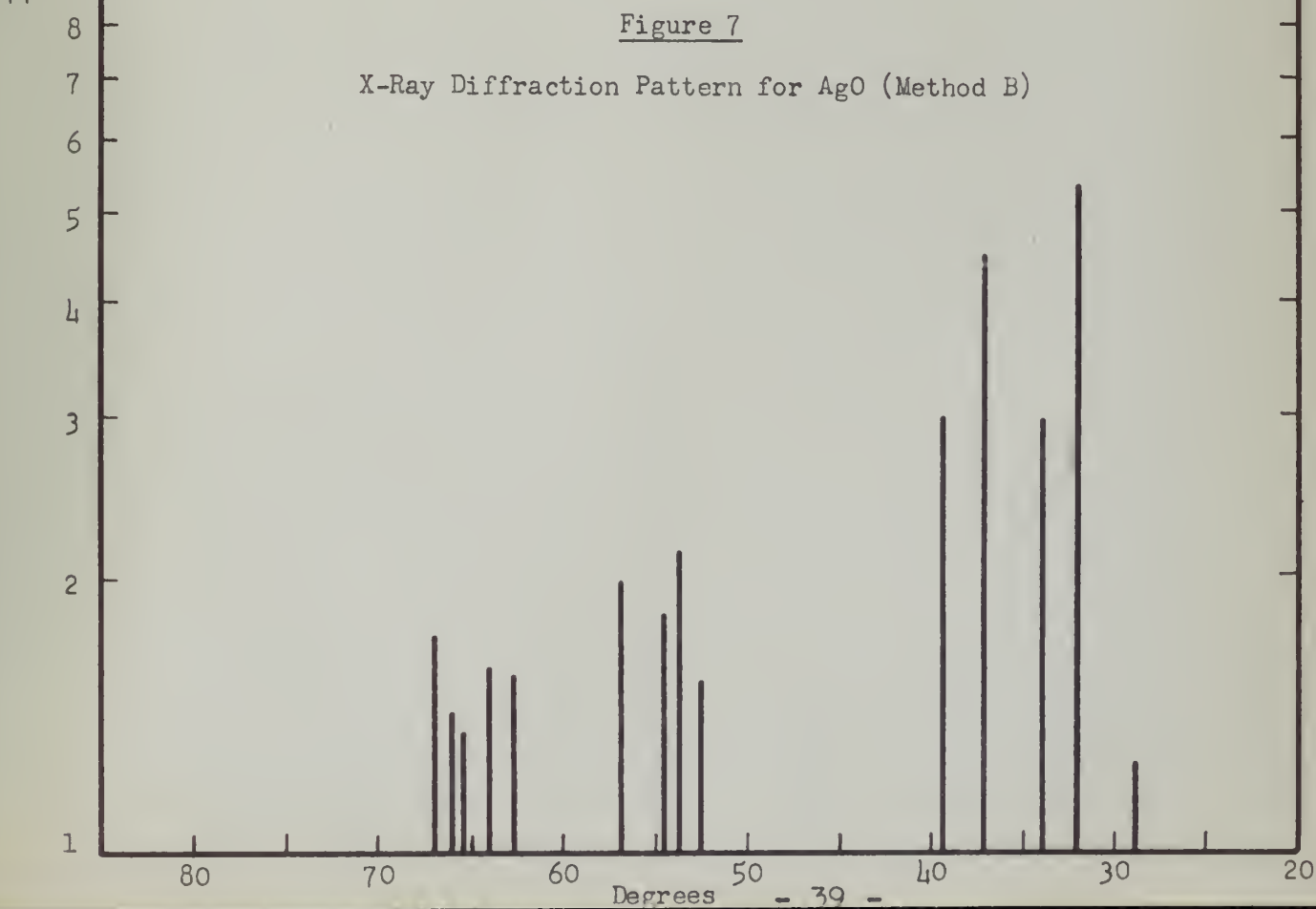
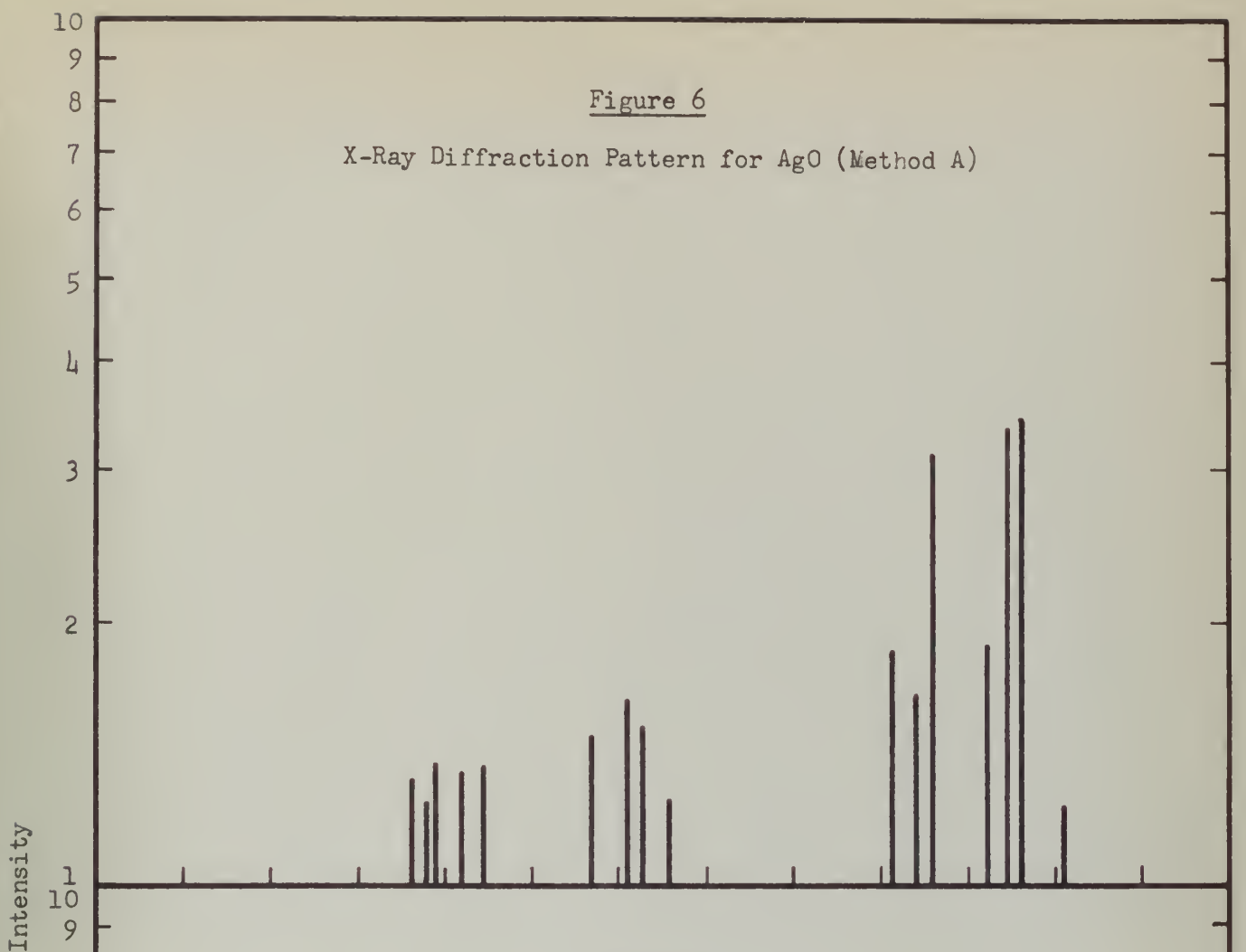
Further study on the silver-oxide-zinc couple is indicated. This study should concern itself with such aspects as the amount of free oxygen adsorbed in the plates at various times during charge and discharge, the evaluation of other separator materials for use in the cell, the evaluation of the life of the cell under extremes of temperature and pressure, the influence of temperature and pressure

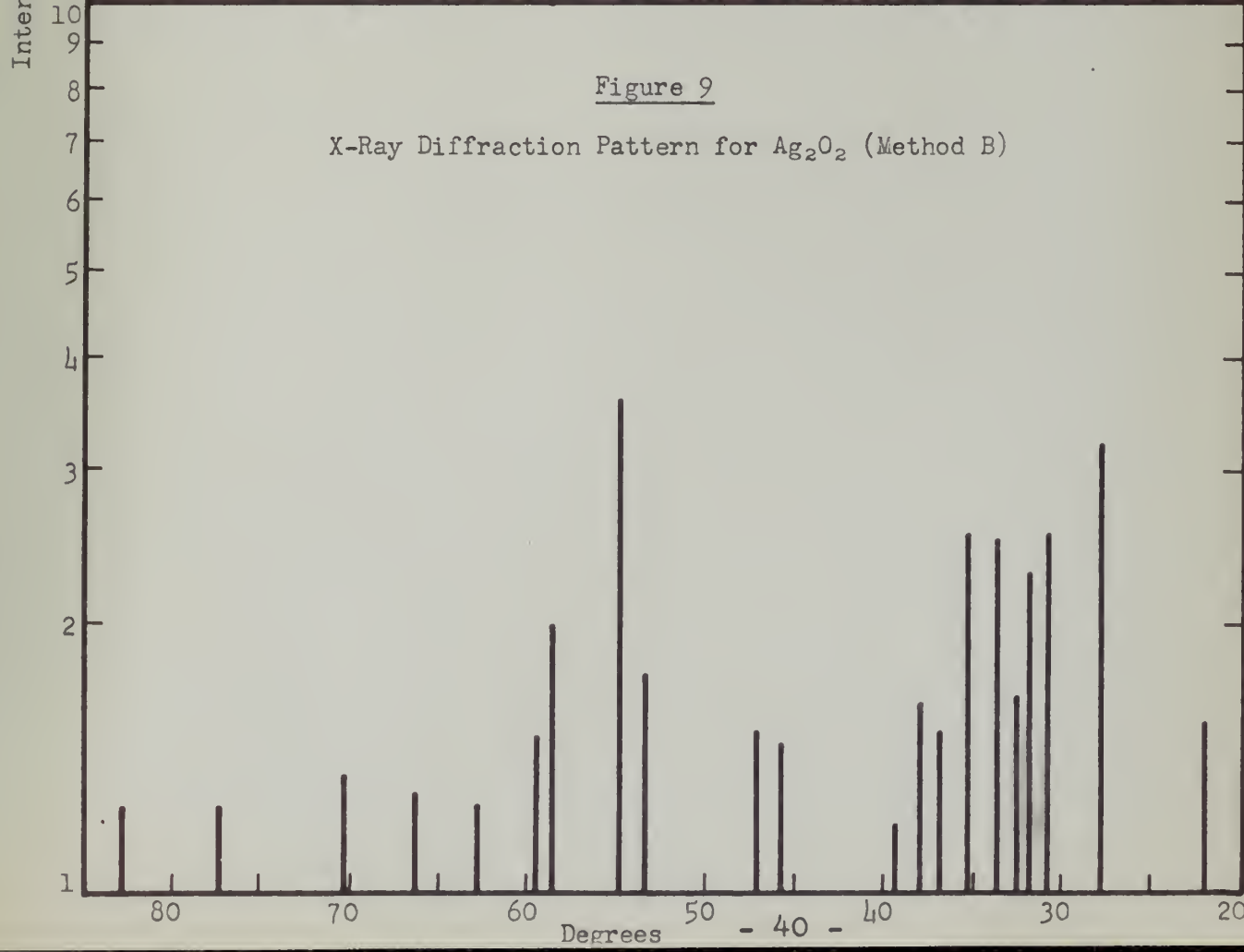
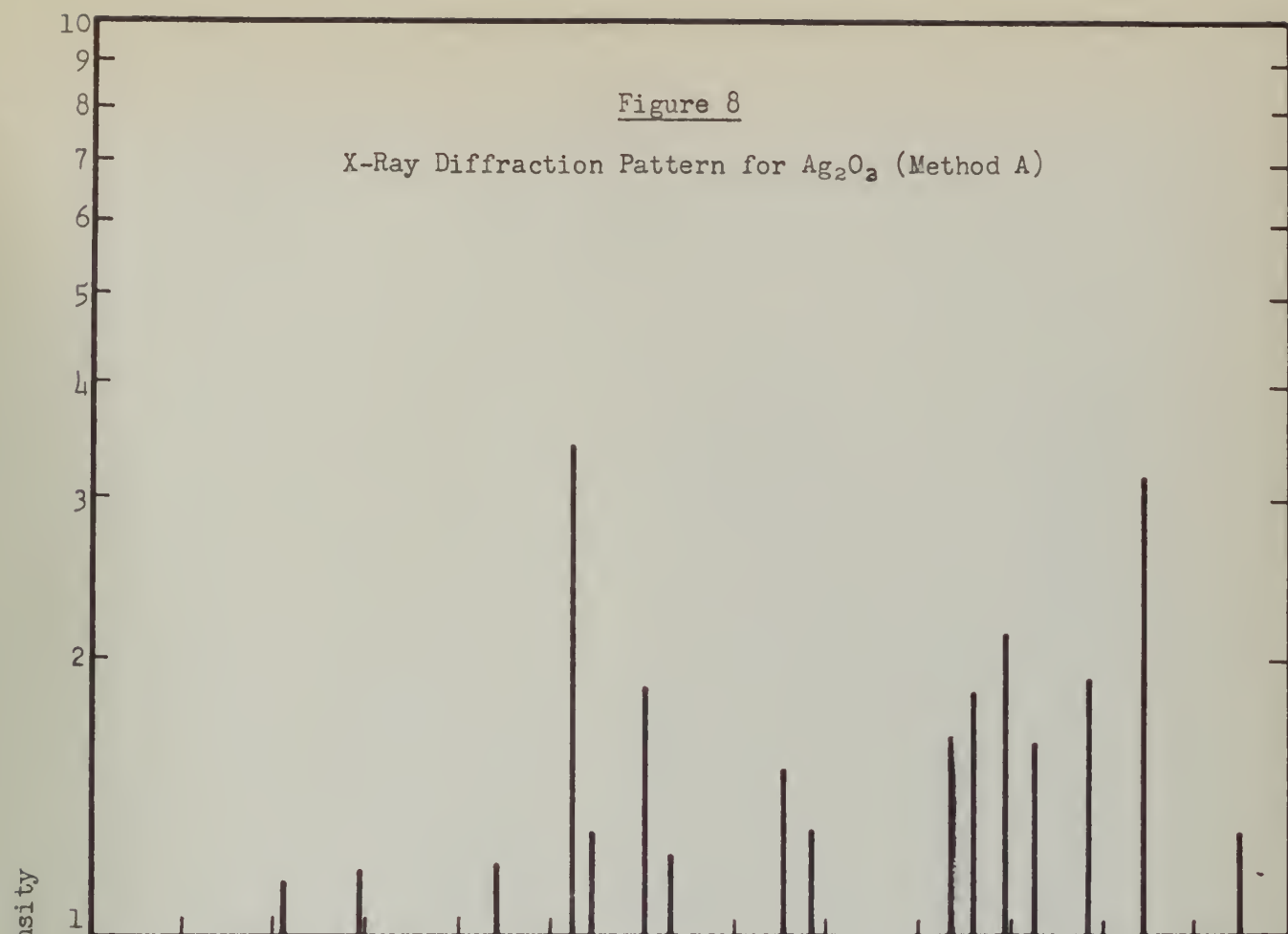
on the capacity of the cell, the improvement of the life of the cell under storage and operating conditions, and the evaluation of a cyclic charging procedure on the gassing of the cell. The use of such a systematic study as found in this study would aid in the further clarification of the performance of the silver cell.

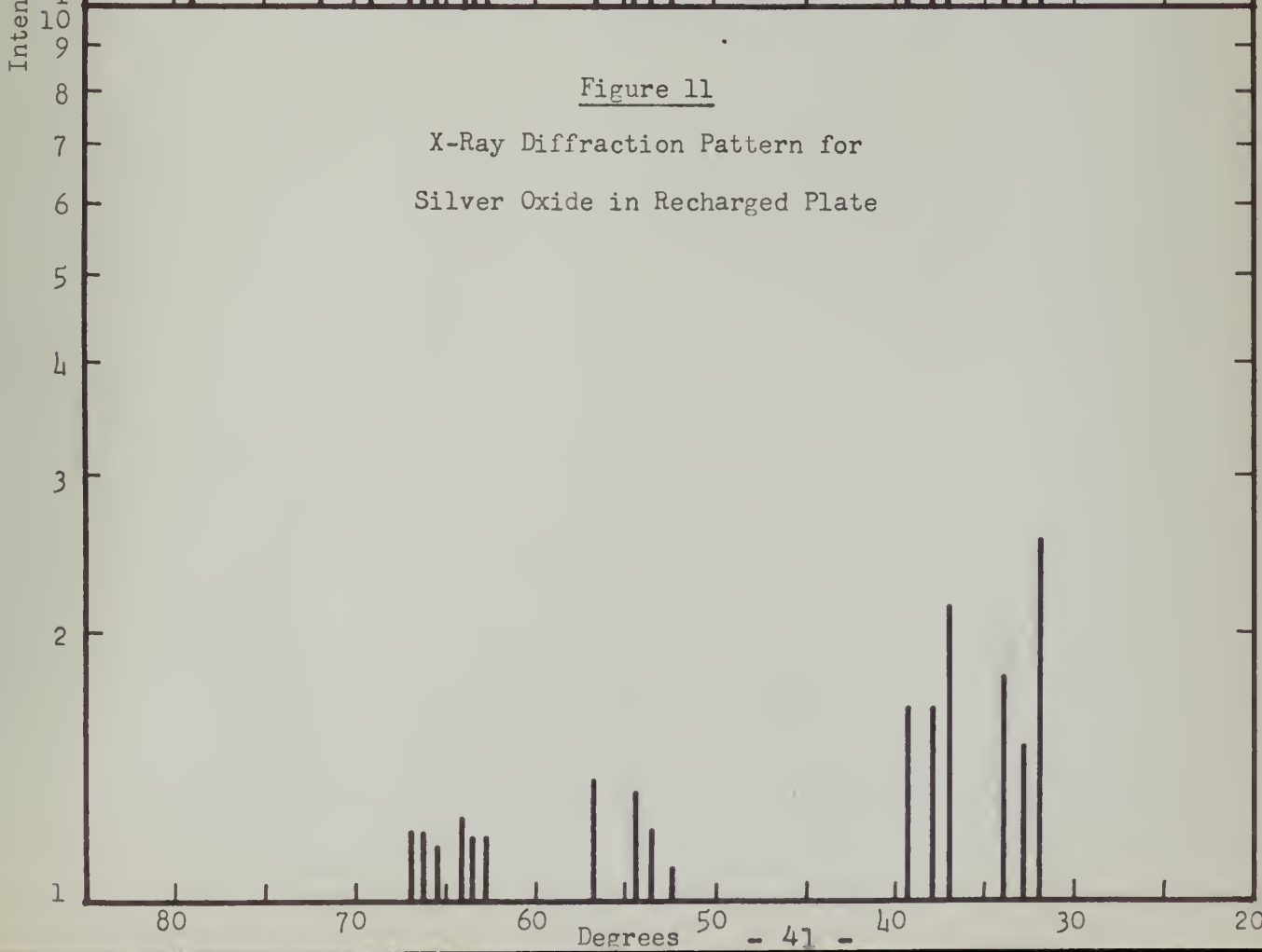
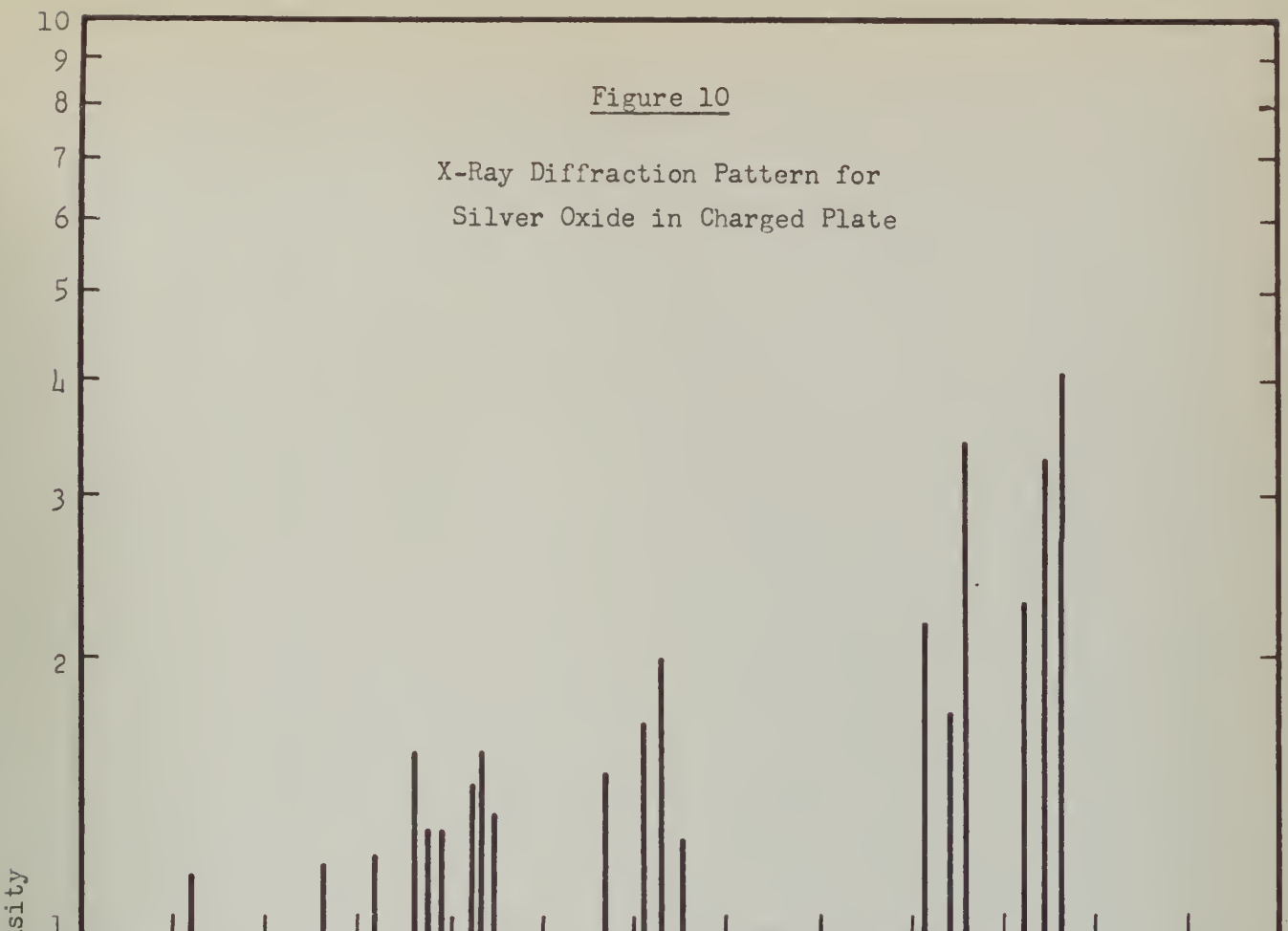
Appendix











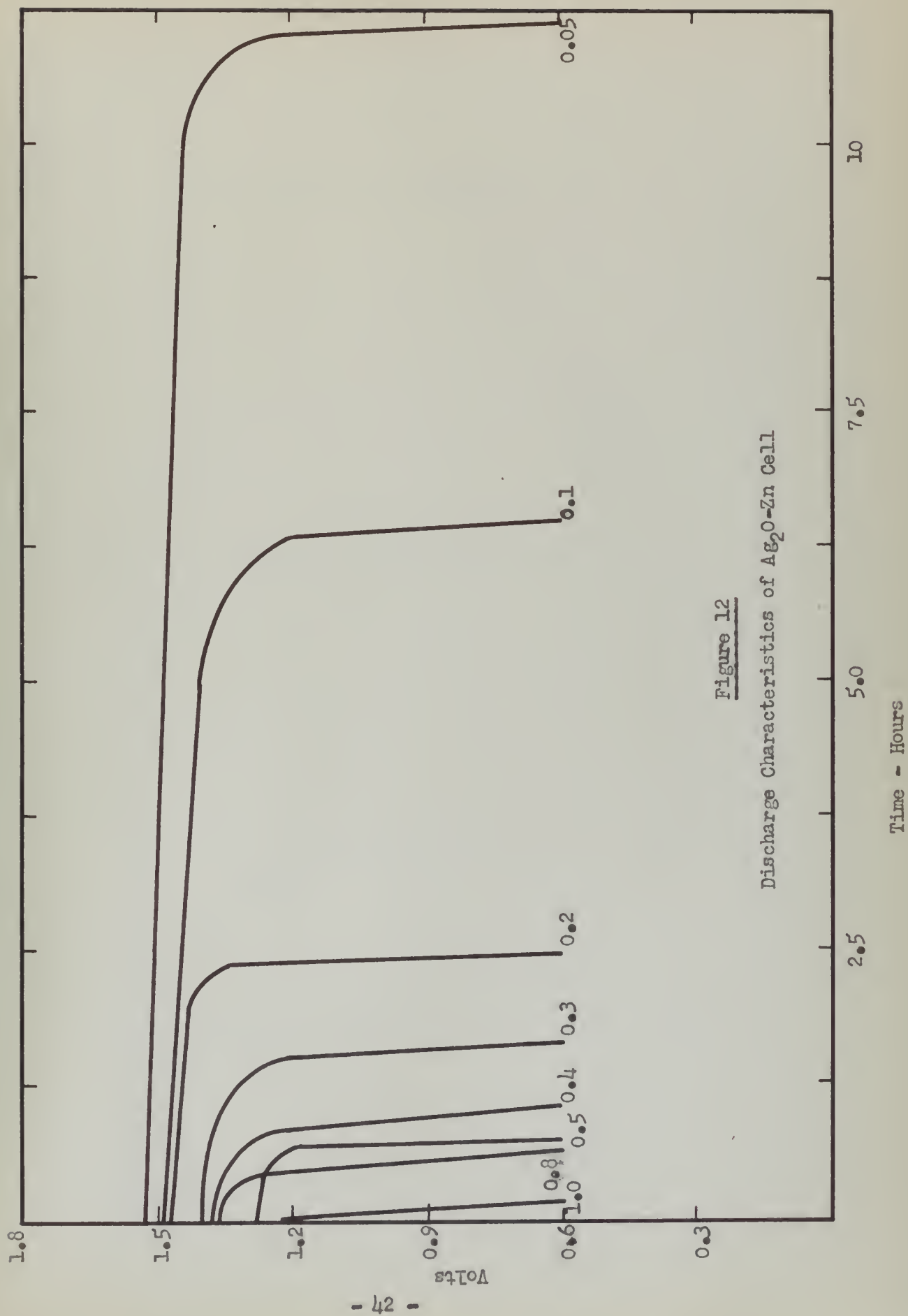
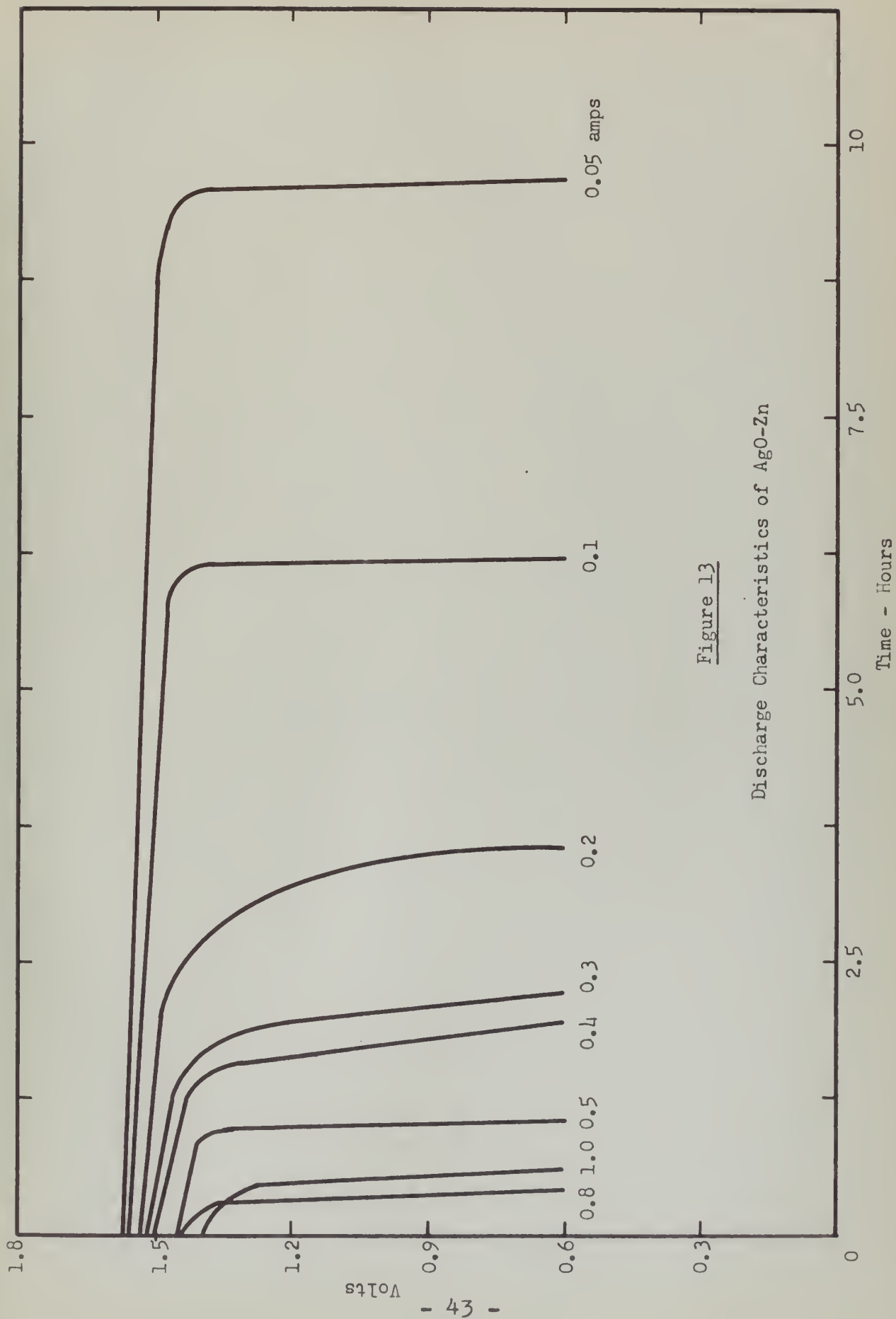


Figure 12
Discharge Characteristics of $\text{Ag}_2\text{O-Zn}$ Cell



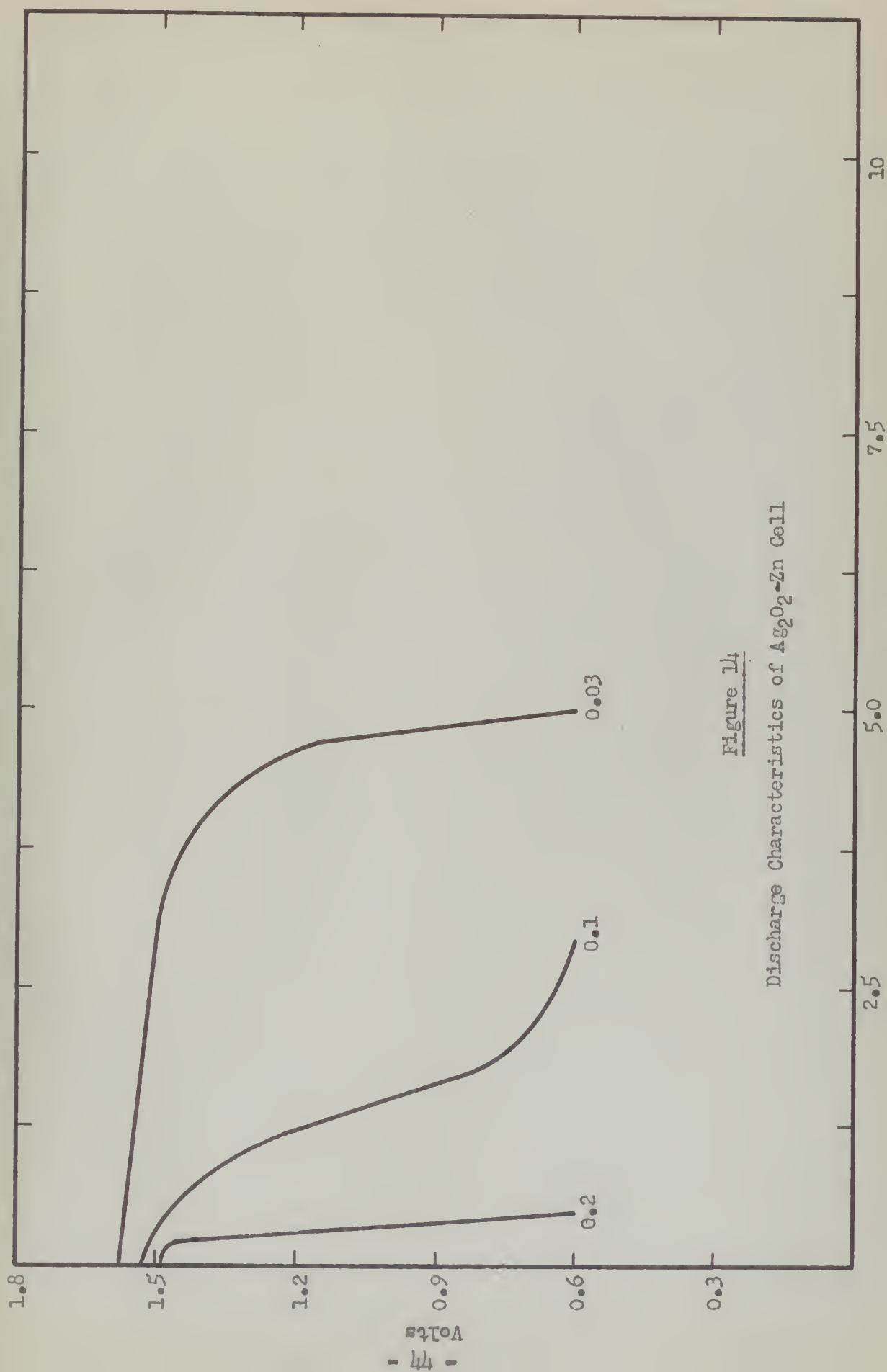


Figure 14
Discharge Characteristics of $\text{Ag}_2\text{O}_2\text{-Zn}$ Cell

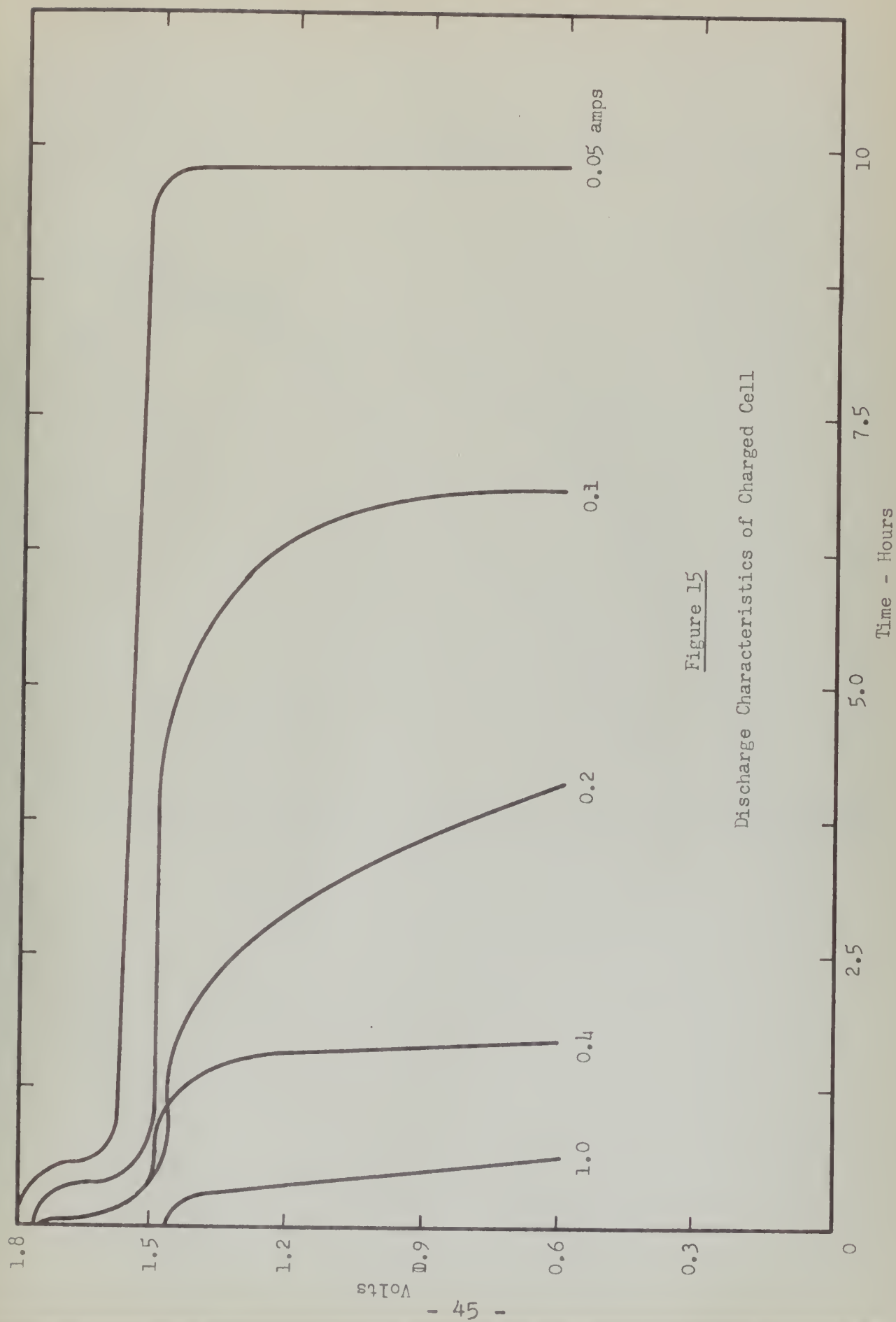


Figure 15
Discharge Characteristics of Charged Cell

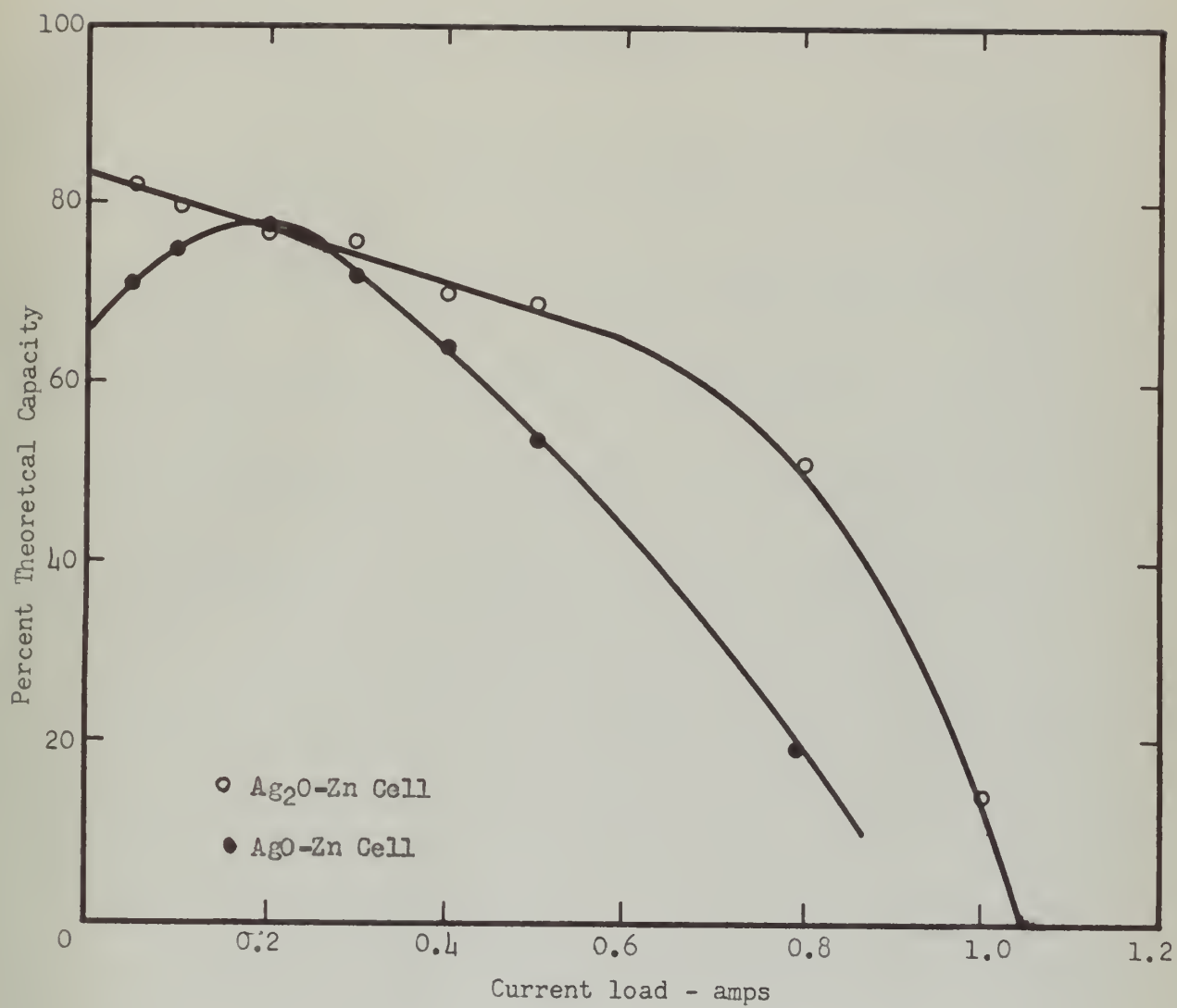


Figure 16

Variation in Percent Capacity with Load

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VITA

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He is associate member of the American Institute of Electrical Engineers, a member of the American Chemical Society, the Electrochemical Society, and the American Rocket Society. He is an associate member of Sigma Xi.

He is married to the former Giovina Mono and they have two children, Mary Margaret, age 6, and William Joseph, age 4.

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